

METHOD AND DEVICE FOR TREATING FUMES GENERATED DURING  
THE PRODUCTION, CONVERSION AND/OR HANDLING OF PRODUCTS  
OF PETROLEUM ORIGIN

5

The present invention relates to the general technical field of the treatment of fumes issuing from products of petroleum origin.

10 In particular, the present invention relates to a method for treating fumes generated during the production, conversion and/or handling of heated products of petroleum origin, advantageously at a temperature of or above 50°C under atmospheric 15 pressure, such as hydrocarbons, asphalts and bituminous mixes. The invention also relates to a device for treating fumes generated during the production, conversion and/or handling of heated products of petroleum origin, suitable for carrying out the method.

20 The present invention also relates to the use of said method or said device in the preparation of an aggregate used in the production of a roadbuilding product, such as a hot mix or a bituminous mix.

25 The production, conversion, handling and/or transport of products of petroleum origin, such as hydrocarbon products, lead to the emission of volatile organic compounds (VOC).

30 In the industry producing products of petroleum origin, such as bituminous products, the main sources of VOC emissions are plants producing hydrocarbon binders (storage tanks, mixers and asphalt loading stations), asphalt plants (storage tanks, asphalt 35 weighers, mixer drainage, transfers of bituminous products), and bituminous product construction sites (spreader: binder spreading; and finisher: unloading of the truck containing hot mixes in the hopper). The VOC

emissions (mainly alkanes, alkenes and aromatic hydrocarbons) are produced by the decomposition of asphaltenes, paraffinic hydrocarbons and sulfur bearing cyclic compounds, and are the main result of the gas-  
5 liquid and liquid-solid reactions which cause emissions of complex chemical compounds.

In order to comply with the forthcoming regulatory and environmental provisions, VOC treatment is one of  
10 the major challenges, particularly in the treatment of releases of products of petroleum origin.

Many methods for treating VOC have heretofore been developed. At present, the main VOC treatment  
15 techniques are adsorption (on granular activated carbon, on activated carbon fabric or on other adsorbents), absorption (by scrubbing with water, oil or other absorbents), thermal oxidation or biological methods.

20 However, while these techniques may be ideal for treating relatively low air flows containing a high VOC concentration, they remain ineffective for treating high throughput effluents with very low VOC  
25 concentrations (about 100 to 1000 ppm), or for treating complex effluents, laden with impurities, as is the case for VOC issuing from products of petroleum origin. Furthermore, adsorption on activated carbon does not permit comprehensive treatment of all the molecular  
30 species included in the fumes (selective adsorption). Moreover, the VOC treatment methods and devices of the prior art mentioned above are generally costly and are still inadequate for handling the high gas flows from a large number of industrial units. In particular, the  
35 activated carbon adsorption technique implies high costs and substantial means for regenerating and upgrading the trapping materials.

In consequence, a need therefore existed, particularly in the field of the treatment of products of petroleum origin, of the bituminous type, to develop a method for treating fumes generated during the 5 production, conversion and/or handling of heated products of petroleum origin, not having the drawbacks of the prior art methods.

The present invention is aimed to fill this need. 10 The applicant has thus discovered a novel method for treating fumes generated during the production, conversion and/or handling of heated products of petroleum origin, permitting the effective treatment of VOC of various types, with a high yield, without 15 generating high olfactory pollution, suitable for complying with present European regulatory and environmental provisions and anticipating those to come, and possibly suitable for recycling the various materials used. The method according to the present 20 invention is also suitable for recycling the granular materials used for trapping the reaction products generated in the treatment reactor, when the device for trapping said products comprises a fluidized bed of granular materials.

25

Moreover, the method according to the present invention is suitable for the efficient treatment of VOC, because it comprises several treatment levels. The method thereby allows a chemical modification of 30 the fume components to be treated by oxidation due to the active species formed in the plasma reactor outside equilibrium (ozone, excited molecular and atomic oxygens). The method according to the present invention is also suitable for trapping the reaction 35 products generated in the reactor from free radical entities using at least one appropriate trapping device. Finally, the method according to the present invention advantageously provides a means for

introducing the fumes by Venturi effect. This serves to change the speed of the gases to be treated and, by the negative pressure zone, to blend the fumes with the dielectric discharge gases in the reactor. The method 5 thereby protects the dielectric discharge zone from any deposits and promotes the mixing necessary for free radical formation.

The subject of the present invention is thus a 10 method for treating fumes generated during the production, conversion and/or handling of heated products of petroleum origin, such as hydrocarbons, asphalts and bituminous hot mixes, characterized in that it implies:

15 - the introduction of said fumes into a reactor in which the fume components undergo free radical degradation by cold plasma generated in the reactor by the introduction of air through at least one dielectric barrier discharge arranged close to at least one of the 20 reactor walls which extend parallel to the flow direction of the fumes passing through the reactor, and - the retention of the reaction products generated in the reactor from the free radical entities resulting from the degradation of the fume components, using at 25 least one appropriate trapping device.

In a particular embodiment of the present invention, the fumes are introduced by a carrier air stream.

30 Advantageously according to the present invention, at least one dielectric barrier discharge is arranged at at least one of the reactor walls which extend parallel to the flow direction of the fumes passing 35 through the reactor.

In a particular embodiment of the present invention, at least one dielectric barrier discharge is present close to each side wall of the reactor.

5 Advantageously according to the present invention, at least one dielectric barrier discharge is arranged at each side wall of the reactor.

10 According to a particular feature of the present invention, the trapping device comprises at least one fluidized bed of an advantageously mineral medium.

15 In a particular embodiment of the present invention, said medium is a granular material advantageously containing alumina, silica, or calcite. In a particular embodiment of the present invention, said medium is a microporous granular material such as zeolite or pumice. In another particular embodiment of the present invention, said medium is a basic granular 20 material such as pozzolan or a carbonate type rock.

According to a particular feature of the present invention, the size of said medium is between 0.5 mm and 20 mm, advantageously between 1 mm and 10 mm.

25 Advantageously according to the present invention, the fluidized bed is fixed or circulating.

30 In a particular embodiment of the present invention, another dielectric barrier discharge is located close to the reactor outlet, advantageously placed perpendicular to the flow direction of the fumes passing through the reactor.

35 In a particular embodiment, the method according to the present invention further comprises, at the reactor outlet, a step of degradation of the residual

ozone formed in the reactor by the passage of the air through the dielectric barrier discharge(s).

In a particular embodiment, the method according  
5 to the present invention further comprises an at least  
partial recirculation of the purified gases located in  
the gas stream leaving the reactor to the reactor  
inlet, in a mixture with the fumes to be treated.

10 The present invention also relates to a device for  
treating fumes generated during the production,  
conversion and/or handling of heated products of  
petroleum origin, such as hydrocarbons, asphalts and  
bituminous hot mixes, in a reactor (1) comprising:

15 - at least one fume introduction system (2) in the  
lower part of the reactor (1),  
- at least one dielectric discharge member (3)  
replacing at least part of at least one of the reactor  
walls (1) which extend parallel to the flow direction  
20 of the fumes passing through the reactor,  
- at least one system for introducing air (4)  
through said dielectric discharge member(s),  
- at least one appropriate trapping device (5) for  
retaining the reaction products generated in the  
25 reactor, and  
- at least one discharge stack (6).

In a particular embodiment of the present  
invention, the fume introduction system (2) contains a  
30 Venturi (2').

In a particular embodiment of the present  
invention, the dielectric discharge member(s) (3) is  
(are) made in the form of modulable cassettes each  
35 consisting of a plurality of parallel electric tubes  
(7), said electric tubes each consisting of electric  
wires (8) sheathed in a dielectric insulation (9) and  
supplied by a high voltage generator.

In a particular embodiment of the present invention, the electric wires (8) are of copper.

5 In a particular embodiment of the present invention, the dielectric insulation (9) is of quartz, ceramic or glass.

10 In a particular embodiment of the present invention, the diameter of the dielectric insulation sheath (9) is between 2 and 10 mm.

15 According to a particular feature of the present invention, the space between the parallel electric tubes (7) is between 1 and 2 mm.

20 According to a particular feature of the present invention, at least one dielectric discharge member (3) is present to replace at least part of each side wall of the reactor (1), said members (3) being advantageously arranged in a face-to-face layout.

25 Advantageously according to the present invention, the trapping device (5) comprises at least one fluidized bed of an advantageously mineral medium.

30 In a particular embodiment, the device according to the present invention further comprises at least one filter means (10, 11) in the upper part of the reactor (1) before the discharge stack (6).

35 In a particular embodiment, the device according to the present invention further comprises at least one dielectric discharge member (3), in the upper part of the reactor (1), before the discharge stack (6).

The present invention also relates to the use of the method or device described above, in which the

trapping device (5) comprises at least one fluidized bed of granular materials, in the preparation of an aggregate used in the production of a roadbuilding material.

5

In a particular embodiment, the roadbuilding product is a hot mix or a bituminous mix.

Various objects and advantages of the present  
10 invention will appear to a person skilled in the art  
through the references to the illustrative drawings  
appended hereto:

Figure 1 is a schematic view of a cross section of  
a reactor (1) for treating fumes issuing from products  
15 of petroleum origin according to an embodiment of the  
invention, which comprises a fume introduction system  
(2) containing a Venturi (2'), at least one dielectric  
discharge member (3) arranged at the reactor (1) walls,  
said members being arranged in a face-to-face layout, a  
20 system for introducing air (4) through each of the  
dielectric discharge members, a fluidized bed (5) of  
granular material located above the zone in which the  
dielectric discharge members (3) are arranged, an  
additional dielectric discharge member (3) located  
25 above the fluidized bed (5), two filter means (10, 11),  
and a discharge stack (6).

Figure 2 is a schematic view of dielectric  
discharge members (3), according to an embodiment of  
30 the invention, in the form of cassettes each consisting  
of a plurality of parallel electric tubes (7), said  
electric tubes each consisting of electric wires (8)  
sheathed in a dielectric insulation (9) and supplied by  
a high voltage generator.

35

The method according to the present invention is  
suitable for efficiently treating various types of  
volatile organic compounds (VOC) issuing from the

production, conversion, handling and/or transport of products of petroleum origin, such as hydrocarbons, asphalts, bituminous mixes, and also fuel oil fumes, generated in particular by aggregate drying operations.

5

The fumes containing VOC are generally emitted when the products of petroleum origin are heated, advantageously between 50 and 250°C, more particularly between 50 and 180°C, even more advantageously between 10 100 and 180°C, under atmospheric pressure. The fumes generally appear during hot contact of the products of petroleum origin with air or with a material at ambient temperature. The fume liberation temperature depends on the types of product of petroleum origin treated. 15 Thus, typically, a fume release is observed above 50°C for epoxy asphalts, and at about 250°C for hot mixes, of the type of hot asphalt mixes or "gußasphalts" in Germany.

20 The fumes to be treated are generally introduced in the lower part of the reactor, preferably at the base of the reactor. Advantageously according to the invention, the fumes are introduced by a carrier air stream. The fumes are thereby introduced by suction 25 into the reactor, with the suction air stream necessary for their transfer. A negative pressure is thereby created in the fume introduction system, particularly by means of a Venturi effect or a fan. The Venturi effect is advantageously created using baffles, 30 preferably placed in or close to the fume introduction system. The fumes to be treated thereby enter into contact and are mixed with the active species of the dielectric discharge.

35 The method according to the present invention is suitable first for ensuring a chemical modification of the fume components to be treated by the species produced by the discharge in the reactor by the passage

of air through the dielectric barrier discharge(s). The active species of the discharge, including ozone and excited oxygenated species, favor the combustion of the lighter species to be treated and the free radical degradation of the heavier species. The excited oxygen (atomic, molecular oxygen) and the ozone, which are powerful oxidants, promote the reactivity of the medium, and oxidation thereby serves to fragment the heavier hydrocarbons. In general, the free radicals formed lead to polymerization of the free radical organic molecules, and polymerization generally takes place on the trapping device.

Advantageously according to the present invention, the negative pressure zone created by the Venturi effect in the fume introduction system in the lower part of the reactor permits the direct introduction of atmospheric air into the reactor through the dielectric barrier discharge(s). Supplementary air injection devices can optionally be arranged in the neighborhood of the outer walls of the reactor, to provide air passages through the dielectric barrier discharge(s). Air can thereby optionally be introduced forcibly by a compressor or a blower in the effluent upflow to be treated.

At least one dielectric barrier discharge is present close to at least one of the reactor walls according to the present invention, and advantageously close to each reactor side wall. The dielectric barrier discharges are advantageously present immediately adjacent to the reactor side walls, or may even be arranged at or on the reactor walls. The dielectric barrier discharges may also be located at a longer distance near the reactor side walls.

According to a preferred embodiment of the invention, the dielectric discharge member(s) (3)

replace at least part of the reactor wall(s). According to another preferred embodiment of the invention, the dielectric discharge member(s) (3) replace the reactor side wall(s). A hole is thereby 5 formed in the wall(s) or in at least part of the wall(s) to insert the dielectric discharge member(s) (3) in said wall(s). In an embodiment of the present invention, several dielectric barrier discharges may be positioned on each reactor wall or instead of each 10 reactor wall. In this case, the dielectric barrier discharges are advantageously located above one another on each wall or behind one another.

After chemical modification of the fume components 15 to be treated by the active species of the discharges such as ozone, the method according to the present invention serves to retain the reaction products generated in the reactor from the free radical entities resulting from the degradation of the fume components, 20 using at least one appropriate trapping device.

In a particular embodiment of the present invention, the trapping device comprises at least one fluidized bed of a solid medium. The solid medium may 25 be selected from the group consisting of aggregates, glass, and mixtures thereof. The solid medium according to the present invention is advantageously a granular material, which may be inorganic, organic, or a mixture of inorganic and organic materials. As an example of 30 an organic medium, mention can be made of media based on rubber or recycle polymers such as polypropylene or polyethylene. Advantageously according to the present invention, the solid medium is a mineral granular material, preferably selected from the group consisting 35 of alumina, silica and calcite. In a particular embodiment of the present invention, the solid medium is a microporous granular material, advantageously mineral, such as zeolite or pumice. The reaction

products generated in the reactor from the free radical entities resulting from the degradation of the fume components being generally acidic, the solid medium according to the invention advantageously has a high 5 acid neutralization capacity. The medium may thereby be a basic material, advantageously mineral, such as pozzolan or a carbonate type rock.

Advantageously according to the present invention, 10 the size of said medium is between 0.5 mm and 20 mm, advantageously between 0.5 mm and 10 mm, even more advantageously between 1 mm and 10 mm.

The trapping device may be loaded or unloaded 15 continuously, thereby permitting continuous treatment of the products of petroleum origin to be degraded. According to a particular feature of the present invention, the trapping device comprises at least one fluidized bed which is fixed or circulating. The 20 fluidized bed according to the invention may thus be a circulating bed, permitting the continuous injection of solid particles into the fluid and avoiding any risk of caking of the particles during the deposits of the trapped polymer.

25

Advantageously according to the present invention, the trapping device is arranged perpendicular to the flow direction of the fumes to be treated passing through the reactor, preferably above the zone where 30 the cold plasma is generated, i.e. above the zone where the dielectric discharge member(s) (3) is (are) arranged.

In a particular embodiment of the present 35 invention, an additional dielectric barrier discharge is located close to the reactor outlet, advantageously placed perpendicular to the flow direction of the fumes passing through the reactor, even more advantageously

above the trapping device (5), to permit a supplementary treatment to the dielectric barrier discharges arranged close to the reactor walls which extend parallel to the flow direction of the fumes to 5 be treated.

Advantageously according to the present invention, the method further comprises, at the reactor outlet, a step of degradation of the residual ozone formed in the 10 reactor by the passage of air through the dielectric barrier discharge(s). This residual ozone degradation step can be carried out using a filter placed at the reactor outlet, such as a metal grille, particularly a copper grille which can be heated to a temperature of 15 about 50°C to 70°C, typically about 60°C. Another filter means, such as quartz fabric, advantageously placed at the reactor outlet, may be used as a means for trapping VOC residues or other compounds to be degraded.

20

Advantageously according to the present invention, the method may also comprise an at least partial recirculation of the purified gases located in the gas 25 stream leaving the reactor, either toward the reactor inlet, in a mixture with the fumes to be treated, or toward the dielectric barrier discharge(s) arranged in the neighborhood of the reactor walls.

The device according to the present invention, 30 which is suitable for carrying out the method of the invention, contains a reactor (1) comprising:

- at least one fume introduction system (2) advantageously containing a Venturi system, in the lower part of the reactor (1), advantageously at the 35 base of the reactor,
- at least one dielectric discharge member (3) arranged to replace at least part of at least one of the

reactor (1) walls which extend parallel to the flow direction of the fumes passing through the reactor,

- at least one system for introducing air (4) through said dielectric discharge member(s),
- 5     • at least one appropriate trapping device (5) for retaining the reaction products generated in the reactor, and
- at least one discharge stack (6).

10       Advantageously according to the present invention, the dielectric discharge member(s) (3) is (are) made in the form of modulable cassettes each consisting of a plurality of parallel electric tubes (7), said electric tubes each consisting of electric wires (8), such as 15 copper wires, sheathed in a dielectric insulation (9) and supplied by a high voltage generator. The direction of the parallel electric tubes (7) of the cassettes may be that of the vertical axis of the reactor (1) or the direction perpendicular to the 20 vertical axis of the reactor (1).

In the context of the present invention, the term "modulable cassettes" means the fact that several cassettes may be arranged on at least one reactor wall 25 - or instead of at least part of at least one reactor wall - to increase the efficiency of the method. The cassettes are thereby advantageously placed either behind one another, to increase the total capacity of the cassettes, or above one another to increase the 30 residence time of the fumes in contact with the plasma generated in the reactor.

In a particular embodiment of the present invention, the electric wires (8) are connected to the 35 edges of the frame of the cassettes, which are advantageously square (Figure 2). Typically, the cassettes according to the present invention have a surface area of  $50 \times 50 \text{ cm}^2$  or of  $20 \times 20 \text{ cm}^2$ , the

impedance of the cassettes being matched to the electric power source (voltage, frequency, current).

5        The dielectric insulation sheaths (9) of the conducting tubes (7) are generally arranged around electric wires (8), thereby providing a uniform diffusion of the plasma in the reactor (1), the air being ionized on the edges of the dielectrics. The dielectric barrier discharges are generally created in  
10      the interstices between the parallel electric tubes (7). The dielectric insulation may be of quartz, ceramic or glass. The diameter of the electric wire (8) is advantageously about 1 to 2 mm. The capacity of the high voltage generator is typically about 1 to 20  
15      kW, advantageously between 1 and 10 kW, even more advantageously between 5 and 10 kW. The voltage of such a generator is typically between 10 and 40 kV, and its frequency is 1 to 20 kHz.

20       The diameter of the dielectric insulation sheath (9) is typically between 2 and 10 mm, advantageously between 2 to 8 mm, even more advantageously between 2 and 5 mm. The space between the parallel electric tubes (7) is typically between 1 and 2 mm.

25       The device according to the present invention advantageously further comprises at least one filter means (10, 11) in the upper part of the reactor (1), before the discharge stack (6), static or dynamic, 30 which may be a metal grille (11) such as a copper grille which can be heated, particularly to remove the residual ozone, and/or a mineral filter such as a glass fiber or quartz fabric filter (10), particularly for trapping residual VOC.

35       In a particular embodiment according to the present invention, the trapping device (5) comprises at least one fluidized bed of granular materials. The

device and the method according to the present invention can then be used for producing aggregates to produce a roadbuilding product. The aggregates are then coated in the reaction products (generally 5 products of the polymer type) generated in the reactor from the free radical entities resulting from the degradation of the fume compounds, and the aggregates can then be reused or recycled for roadbuilding 10 applications. The device and the method according to the present invention can thereby be used for the production of a hot mix or a bituminous mix, by mixing the coated aggregates as obtained by the present 15 invention with an asphalt-based mixture.

15 The following nonlimiting example illustrates the present invention.

**Embodiment of the invention:**

20 A device according to the present invention comprises a reactor (1) with a rectangular base, equipped with a fume introduction system (2) with Venturi, two dielectric discharge members (3) replacing part of each side wall of the reactor (1) and arranged 25 parallel to the gas flow, a system for injecting dry air (4) through said dielectric discharge members, a trapping device (5) consisting of a fluidized bed of a pozzolan aggregate, a mineral filter which collects the residual VOC and a discharge stack (6).

30 Such a device was used to purify products such as asphalt fumes containing VOC, of which the initial contents of the effluents were 5 kg/hour. The operation of the device for two hours served to remove 35 80 to 90% of the effluents on the mineral filter using appropriate treatment, with a gas-VOC mixture and excited species of the discharge by Venturi effect.